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## EFFECT OF THE NATURE OF CARBON NANOTUBES ON THE STRUCTURE AND STRENGTH OF CERAMIC COMPOSITES

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A composite material based on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and two types of carbon nanotubes obtained from a methane-hydrogen mixture and propane-butane mixture was synthesized. The results of vacuum sintering and a comparative analysis of the structure of the material obtained as a function of the type of nanotubes and their content 3 – 24 vol.% are presented. A composite material with equal crystallite structure and uniform distribution of nanotubes in the matrix, demonstrating an increase in strength in bending to 400 MPa, is obtained.

**Key words:** composite material, ceramic, aluminum oxide, carbon nanotubes, vacuum firing, strength in bending.

Ceramic materials are widely used for manufacturing articles used in construction. However, because ceramic materials are highly brittle compared with, for example, metals the use of ceramics is limited in many avenues. To overcome this drawback solid particles of different kinds and shapes are included in the material. Such reinforcing inclusions are usually glass or carbon fibers, including nanotubes [1 – 3].

Among the reinforcing materials used carbon nanotubes stand out sharply by their structure and unsurpassed mechanical properties, which can improve the characteristics of a polycrystalline ceramic matrix, such as, for example, the hardness, strength, Young's modulus, impact toughness and durability [4 – 6].

One of the most promising types of ceramic material is ceramic based on Al<sub>2</sub>O<sub>3</sub>. This type of ceramic is widely used in industry, for example, in aerospace (as construction and insulating components) and in other applications elsewhere special inertness and strength is required of the materials used.

It is reported in the literature on reinforcing an Al<sub>2</sub>O<sub>3</sub> ceramic matrix with carbon nanotubes that the strength in-

creases by different degrees. For example, in [4, 7] the cracking resistance of ceramic composites improved by up to 200%. The results of a study of the possible mechanisms by which carbon nanotubes slow down and even stop crack growth in such materials are presented in [8 – 10].

The presence of carbon nanotubes in an Al<sub>2</sub>O<sub>3</sub> matrix lowers the density of the sintered composite material by means of their own low density and also decreases the size of the grains of the polycrystalline matrix by creating a physical limiting barrier, which stops further grain growth in the presence of possible recrystallization [4, 9]. In addition, the improvement in the mechanical properties of composite materials is associated with the formation of so-called 'bridges' and 'anchors' from carbon nanotubes between the edges of the cracks formed [8]. Other known mechanisms are the drawing and rupture of nanotubes when cracks appear and propagate and the deviation of cracks from a straight propagation path [10].

The ultimate strengthening effect depends on the strength of the bond between the phases of the composite material and the corresponding effectiveness of the load distribution between the carbon nanotubes and the Al<sub>2</sub>O<sub>3</sub> ceramic matrix. Here the dispersity and structure of the carbon material are important. Single-layer carbon nanotubes possess the best mechanical properties, but because of inadequate thermal stability they do not withstand the prolonged heating and

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**Fig. 1.** TEM images of carbon nanotubes obtained from propane-butane (*a*) and methane-hydrogen (*b*) mixtures.

high-temperature pressing during the production of ceramic materials. Multilayer carbon nanotubes are more stable and nanodefects in their outer walls make possible better adhesion with the  $\text{Al}_2\text{O}_3$  matrix.

### CARBON NANOTUBES

The multilayer nanotubes used in the present work were obtained at the D. I. Mendeleev Russian Chemical Technology University [11]. These tubes were produced from two types of raw material in a semi-industrial, flow-through, augur-type reactor with capacity 30 g/h. In the first method of production nanotubes were synthesized by means of pyrolysis of a propane-hydrogen gas mixture with  $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$  as catalyst and additions of cobalt and molybdenum compounds. The second method consisted of pyrolysis of a methane-hydrogen mixture with the participation of the catalyst  $(\text{Fe}_{0.45}\text{Co}_{0.15}\text{Al}_{0.40})_2\text{O}_3$ . The pyrolysis temperature was 590 – 600°C for the propane-butane and 690 – 720°C for the methane-hydrogen mixture. Both types of nanotubes were used in the present work in a state with residues of the catalyst remaining on the tubes in order to lower the cost of production of the composite material to the commercial level.

The structure of both types of carbon nanotubes was studied. Photographs obtained by means of transmission electron microscopy are presented in Fig. 1.

Both methods of synthesis lead to the formation of a bamboo-like structure of nanotubes with a large number of internal bridges. In the first method the number of layers was 20 – 90 and the diameter was 20 – 150 nm. The structure of the nanotubes produced from the propane-butane gas mixture is nonuniform with distinct nanotubes up to 120 – 150 nm in diameter and the presence of large crystalline graphite formations up to 1  $\mu\text{m}$  in size. These nanotubes differed by a high density of defects in the external layers and the presence of inclusions on the surface.

When the methane-hydrogen gas mixture was used in the synthesis process the number of layers decreased to 8 – 27 and the diameter decreased to 10 – 30 nm. The structure of the nanotubes was distinguished by its uniformity and the content of the residues of catalyst and impurities of amorphous carbon was negligible.

### DISPERSION OF CARBON NANOTUBES

In the production of carbon nanotubes, as a rule, mechanically entangled structures are obtained. These structures spontaneously form aggregates easily and/or even simply become entwined during the growth process. Many different approaches and avenues have been proposed for solving the problem of dispersion of nanotubes: mechanical dispersion in mills, ultrasonic action, functionalization of surfaces and use of surfactants [12]. Usually, ultrasonic action is used in combination with surfactants. The usual alcohol and water solutions are used also. In this respect, water solutions of ethyl alcohol, polyvinyl alcohol, isopropyl alcohol and dimethylformamide have proven to be most effective [10]. These four media were chosen for dispersion of nanotubes in the present work.

Water solutions with 1 vol.% ethyl alcohol, polyvinyl alcohol, isopropyl alcohol and dimethylformamide with the ratio of the amount of nanotubes to the amount of solution equal to 1 : 5 were used. Each solution was irradiated with 22 kHz ultrasound up to the formation of a uniform solution. The treatment time varied from 20 min to 1.5 h. The degree of uniformity was checked visually. The dispersion experiments are described in greater detail in [4, 5].

Comparison of the stability of the suspensions obtained showed that the dimethylformamide solution and the polyvinyl alcohol solution exhibit the longest stability. They did not show any indications of re-aggregation for several weeks. No effects of the method used to obtain nanotubes on the behavior of the suspension during and after dispersion were found.

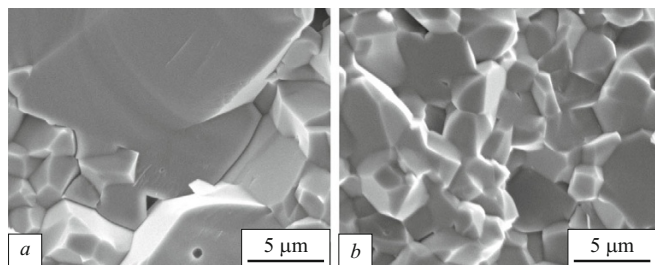
### BATCH PREPARATION AND PRESSING OF BLANKS

The same ceramic technology for preparing and molding the batch irrespective of the type of carbon nanotubes was used to obtain ceramic samples. The suspensions obtained after ultrasonic treatment of carbon nanotubes in water solutions of polyvinyl alcohol and dimethylformamide were mixed with alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) in a planetary mill to attain the best homogenization. The mixing time was 20 – 40 min at 600 rps.

The homogenization of the initial mixture is an important factor influencing the properties of the final composite. Next, the paste-like body obtained was dried in air to a powdered state with residual moisture content 5 – 8%.

The powder obtained was passed through 0.5 and 0.2 mm sieves. Granular powder with 2 – 3  $\mu\text{m}$  particles and carbon nanotube content from 3 to 24 vol.% was obtained at the output.

The samples were molded under pressure 100 MPa. Blanks in the form of rectangular bars and disks were obtained. The molding process showed that in contrast to the water solution of dimethylformamide the water solution of polyvinyl alcohol not only possesses the property of stabili-



**Fig. 2.** SEM images of a composite with carbon nanotubes from a propane-butane mixture (*a*) and a methane-hydrogen mixture (*b*).

zation of a suspension for a long period of time, not allowing bundles of carbon nanotubes to re-aggregate, but it can also assist during pressing of the samples of ceramic composite, playing the role of a process binder.

During the entire process of preparing batch and pressing blanks no differences in behavior were found between the batch using carbon nanotubes from the methane-hydrogen mixture and the batch with nanotubes from the propane-butane mixture.

## VACUUM SINTERING

The samples obtained were sintered in vacuum at residual pressure  $10^{-4}$  mm Hg and different temperatures. In the course of determining the best regime the structure of the nanocomposite was investigated with the aid of optical and scanning electron microscopy in order to determine the grain sizes and the character of the distribution of carbon nanotubes in the samples. Photographs of the samples are displayed in Fig. 2.

The defective walls of the nanotubes, obtained by using a propane-butane gas mixture, manifest higher activity and promote migration of nanotubes during firing. In addition, their arrangement is chaotic and the general reinforcing properties are lost. Most carbon nanotubes of this type are in the region of closed intercrystalline pores. The result is that the composite acquires a nonuniform structure with a large variance of the grain size in the range 5 – 40  $\mu\text{m}$  and residual closed porosity remains. The result of all this is that the ultimate strength in bending is low: 250 – 300 MPa.

**TABLE 1.** Characteristics of Ceramic Samples obtained from  $\alpha\text{-Al}_2\text{O}_3$  and Carbon Nanotubes (CNT) obtained from a Methane-Hydrogen Gas Mixture

CNT content, vol.%	Lineal shrinkage, %	Open porosity, %	Water absorption, %	Apparent density, g/cm <sup>3</sup>
0	16.59	0	0	3.97
3	15.49	0	0	3.85
9	15.18	0.02	0.07	3.74
15	14.06	0.03	0.11	3.67
24	8.67	8.28	24.67	2.97

At the same time, in the samples obtained using carbon nanotubes obtained from a methane-hydrogen mixture the nanotubes are distributed uniformly over the entire volume. The nanotubes form in the ceramic composite a reticular framework along the facets of the crystals of the ceramic matrix, which impedes the growth of corundum crystals and promotes complete removal of the closed porosity and the formation of a dense equi-crystallite material with grain size 3 – 5  $\mu\text{m}$ . The ultimate strength in bending for samples obtained using carbon nanotubes from a methane-hydrogen gas mixture was 350 – 400 MPa.

After studying the effect of the nature of the nanotubes on the quality of the samples obtained all subsequent experiments on obtaining a composite powder and its vacuum sintering were performed using the nanotubes obtained from a methane-hydrogen gas mixture.

Finding a sintering regime is a difficult and time-consuming problem. The firings showed that a special concrete regime must be chosen for each one percentage point of the carbon nanotube content in the samples. It was found that the higher the nanotubes content in a sintered blank, the longer the period of time required to optimize the sintering regime is. As the nanotubes content increases the final sintering temperature increases and therefore the expenditure of time and energy on this process increases.

The best results in terms of the magnitude of the open porosity and water absorption were obtained for samples with nanotube content to 3 vol.% with the maximum sintering temperature 1700°C and two intermediate soakings for 2 and 4 h. The characteristics of samples with nanotubes from methane-hydrogen gas mixture are presented in Table 1.

It is evident from Table 1 that starting with nanotube content 9 – 10 vol.% we were not able to obtain zero porosity and water absorption because of difficulties in finding a sintering regime. As the nanotube content increases to 24 – 25 vol.% this optimization process becomes especially complex. This is due to the activity of the carbon nanotubes during sintering and a corresponding increase of the final temperature and total sintering time of the samples, which ultimately increase the labor and production costs of the composite with a high percentage content of nanotubes.

## CONCLUSIONS

The production of a composite material using two types of carbon nanotubes as the reinforcing element for the corundum matrix was studied. Both types of nanotubes were obtained by pyrolysis of gas mixtures — propane-butane and methane-hydrogen. The corresponding samples of nanotubes exhibit different morphology and properties and differ by the number of layers, integrity of the walls, residual content of the catalyst and amorphous and crystalline carbon.

The effect of ultrasound on the behavior of such nanotubes in water solutions of ethyl alcohol, polypropylene alco-

hol, isopropyl alcohol and dimethylformamide was studied. It was found that water solutions of polyvinyl alcohol and dimethylformamide are the best medium for long-time stabilization of suspensions and prevention of re-aggregation of carbon nanotubes. The polyvinyl alcohol solution is more suitable as a process binder for pressing blanks than the dimethylformamide solution. In the process of dispersion, batch preparation and pressing of blanks no differences associated with the use of different types of carbon nanotubes were found.

It was found that with the use of nanotubes from a propane-butane mixture the defective walls of the nanotubes show higher activity during sintering, which results in grain-size nonuniformities (5 – 40  $\mu\text{m}$ ) and the spatial distribution of the nanotubes. The bulk of the nanotubes is concentrated in the region of the residual closed porosity and does not form a reinforcing structure. The strength in bending of such samples does not exceed 300 MPa.

Conversely, the use of structurally more perfect carbon nanotubes obtained from methane-hydrogen mixtures made it possible to obtain ceramic samples with more uniform morphology, small grain size (3 – 5  $\mu\text{m}$ ) and uniform distribution of the carbon nanotubes over the facets of the crystals, and zero open and closed porosities. The strength of these samples in bending reaches 400 MPa.

The increase in strength and the simultaneous decrease of the density of the material make it possible to use it in the manufacture of structures for different fields of engineering, including the aerospace and automobile industries.

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